

TITLE

SOLID SHEET MATERIAL ESPECIALLY USEFUL FOR CIRCUIT BOARDS

CROSS-REFERENCE TO RELATED APPLICATION

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This application is a division of co-pending application No. 10/227,997, filed August 26, 2002 and claims the benefit of U.S. Provisional Application No. 60/315,890, filed August 30, 2001.

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FIELD OF INVENTION

The field of invention relates to solid sheets comprising thermoplastic polymer having low moisture absorption and high tensile modulus fibers, in which the 15 thermoplastic polymer is the matrix polymer, substrates for circuit boards made therefrom, and methods of making the foregoing.

BACKGROUND

Circuit boards are important items of commerce, 20 being used in virtually every electronic device. The "board" or supporting member of a circuit board or other electronic devices (such as the interposer in a flip-chip package) is an important component of such devices, and properties of the materials used to make such boards are 25 important to the functioning of the electronic or electrical circuit.

As electronic components have become more sophisticated, the demands placed upon the materials used for boards have increased. For example, for many 30 applications it is preferred that the board have a coefficient of expansion which matches those of the chips mounted on the board, and/or that the board have a low dielectric constant, and low dissipation factor, especially when high frequency devices are mounted on the 35 board. These three factors are often adversely affected

by the absorption of moisture by the board materials, which changes the dimensions of the board and/or changes the dielectric constant and/or dissipation factor of the board itself, and/or causes warpage.

5        The simplest boards for relatively nondemanding applications are typically made from a thermoset resin such as an epoxy filled with a fibrous reinforcement such as glass fiber. The glass fiber, often in the form of a woven fabric, is saturated with liquid epoxy resin to  
10      form a "prepreg", which is cured in form of a board. As the demands on boards increase, the glass may be replaced by a higher modulus infusible fiber such as an aramid. However, fibers such as aramid fibers, and epoxy resins, absorb significant amounts of moisture, and so are  
15      sometimes unsuitable for use together in highly demanding circuit board uses. Thus there is a need for improved circuit board materials.

Japanese Patent Application 2000-334871 describes the preparation of a sheet from which a prepreg may be  
20      formed by "laminating" a three layer structure in which the middle layer may be an nonwoven sheet containing synthetic organic fiber and the two outer layers may contain aramids or other infusible fibers. From the way prepreg formation is described, it appears the sheet is  
25      porous.

Japanese Patent Application 11-117184 describes the preparation of a sheet from which a prepreg may be formed by forming a nonwoven sheet from aramid and liquid crystalline polymer (LCP) fibers, heating sheet under  
30      pressure to make the LCP flow, and then adding a thermoset resin to form a prepreg. From the reported densities of the sheets actually made, they are porous.

Japanese Patent Application 9-21089 describes the preparation of an LCP nonwoven sheet (paper) which is

reported to have low moisture absorption. Other fibers can also be present in the sheet. The product, after being heated under pressure to partially consolidate the sheet, is apparently still a paper-like material.

5 Japanese Patent Application 11-229290 describes the preparation of a paper made from LCP and aramid fibers which can be impregnated with an epoxy resin which is then cured. The resulting board may be used as a circuit board. No melting or flow under heat and/or pressure of  
10 the LCP is described.

SUMMARY OF INVENTION

Our invention includes:

15 sheets, comprising (a) a nonwoven sheet of short high tensile modulus fibers, and (b) a thermoplastic polymer having low moisture absorption; the sheet having an apparent density which is at least about 75% of its calculated density.

20 laminates made therefrom;  
circuit boards made therefrom;  
processes for the production of a solid sheet material, comprising heating and applying pressure to, for a sufficient amount of time,:  
25 (a) a multilayer sheet structure, comprising, at least one layer containing a nonwoven sheet of high tensile modulus fiber and at least one other layer, and at least one of said layers present comprises a thermoplastic polymer having low moisture absorption; or  
30 (b) a single layer sheet structure comprising a nonwoven fabric comprising short lengths of a high tensile modulus fiber and a thermoplastic polymer having low moisture absorption;  
to form a sheet having an apparent density of at least about 75% of its calculated density.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

Herein certain terms are used. Some of these are defined below.

5 By a "thermoplastic polymer having low moisture absorption" (TP) is meant a thermoplastic plastic polymer which absorbs less than 1.0 weight percent moisture (based on the weight of the thermoplastic polymer) when measured on a sheet of pure thermoplastic polymer by the  
10 method described below. Preferably the moisture absorption of the thermoplastic polymer is about 0.5 weight percent or less, more preferably about 0.25 weight percent or less, and especially preferably about 0.10 weight percent or less.

15 By "high tensile modulus fibers" (HTMF) are meant these product forms having a tensile modulus of about 10 GPa or more, preferably about 50 GPa or more, more preferably about 70 GPa or more, when measured in accordance with ASTM D885-85 method, using a 1.1 twist  
20 multiplier. HTMF herein include high tensile modulus fibers, fibrils and fibrils, unless it is specifically indicated not all three are included. The HTMFs are synthetic organic materials, and this does not include carbon fibers of any kind.

25 By "LCP" is meant a polymer which is anisotropic when tested by the TOT test as described in U.S. Patent No. 4,118,372, which is hereby incorporated by reference in its entirety. By thermotropic is meant the LCP may be melted and is anisotropic in the melt, as described in  
30 the TOT test.

By "nonwoven HTMF containing or comprising sheet" or "nonwoven HTMF containing or comprising "fabric" or "nonwoven HTMF containing or comprising paper" is meant a nonwoven sheet (or fabric or paper) that contains (or

comprises short HTMFs. In this context herein the words "paper", "sheet" and "fabric" are used interchangeably.

By "nonwoven sheet" herein is meant a nonwoven "fabric" formed by any number of different methods, for 5 example wet lay of short fibers (often called a paper), dry lay, flash spun, melt spun, mechanically needled felt, spunlaced. A preferred form of nonwoven sheet is a paper as described in U.S. Patent Nos. 4,886,578 and 3,756,908, each of which is hereby incorporated by 10 reference in its entirety. These patents describe aramid papers, but other HTMFs may also be similarly used. This process also includes the optional use of a binder, wherein such binders include, but are not limited to, aramid fibrils and other binders known within the 15 industry. Dry-lay methods of manufacturing which are well known within the art are described by U.S. Patent No. 3,620,903 which is hereby incorporated by reference in its entirety.

By "fiber" is meant an object having a length and a 20 maximum cross-sectional dimension, the maximum cross sectional dimension typically being in the range of about 0.3  $\mu\text{m}$  to about 100 $\mu\text{m}$  and an aspect ratio (length/width) of  $\geq 50$ .

By "aramid fiber" herein is meant aromatic polyamide 25 fiber, wherein at least 85% of the amide (-CONH-) linkages are attached directly to two aromatic rings. Optionally, additives can be used with the aramid and dispersed throughout the polyfiber structure, and it has been found that up to as much as about 10 percent by 30 weight of other polymeric material can be blended with the aramid. It has also been found that copolymers can be used having as much as about 10 percent of other diamines substituted for the diamine of the aramid or as much as

about 10 percent of other diacid chlorides substituted for the diacid chloride of the aramid.

By "fibrils" herein is meant a fiber-like material having a diameter of about 0.1  $\mu\text{m}$  to about 25  $\mu\text{m}$ , and an 5 aspect ratio of 3 to about 100.

By "fibrids" herein is meant very small, nongranular, fibrous or film-like particles with at least one of their three dimensions to be of minor magnitude relative to the largest dimension. These particles are 10 prepared by precipitation of a solution of polymeric material using a non-solvent under high shear.

The term "aramid fibrids", as used herein, means non-granular film-like particles of aromatic polyamide having a melting point or decomposition point above 15 320°C. The aramid fibrids typically have an average length in the range of about 0.2 mm to about 1 mm with an aspect ratio of about 5 to about 10. The thickness dimension is on the order of a fraction of a micrometer, for example about 0.1  $\mu\text{m}$  to about 1.0  $\mu\text{m}$ . In addition to 20 aromatic polyamide, aramid fibrids may optionally additionally comprise one or more of dyes, pigments or other additives such as those described in U.S. Patent Nos. 5,965,072 and 5,998,309, each of which is hereby incorporated by reference in its entirety.

25 By "short fibers" or "short lengths" of fibers herein is meant fibers with an aspect ratio of less than about 2000, preferably about 200-1000 and more preferably about 250-600.

By "powder" herein is meant a material having an 30 aspect ratio of less than 3. These particles typically have a maximum dimension of about 5  $\mu\text{m}$  to about 1000  $\mu\text{m}$ . Powder particles may have smooth or rough textured surfaces and may comprise fibrils attached to a "central core" section.

By "apparent density" is meant the overall volume of a piece of a sheet calculated as follows. Measuring thickness (if somewhat uneven, an average value should be determined), length and width, and multiplying these 5 values to obtain a volume. The sheet is weighed in air. This weight is then divided by the volume to obtain an apparent density. A sheet which is porous will have an apparent density lower than its calculated density.

By "calculated density" is meant the density of an 10 object, assuming it has no voids or pores, which is calculated from the amounts and densities of the individual materials in that object. For example, if an object was 60 weight percent of a material having a density of 1.4, and 40 weight percent of a material 15 having a density of 1.6, the calculated density of that object would be:

$$d = 1.0 / [(0.6/1.4) + (0.4/1.6)] = 1.47$$

Calculations of this type are well known in the art.

By "solid" herein is meant that the material has an 20 apparent density which is at least about 75% of its calculated density.

By "a" or "an" herein, such as a TP or HTMF is meant one or more.

By "comprising" herein is meant the named items 25 (materials), and any other additional materials or compositions may be present.

Preferred "solid" or "consolidated" sheets are now described.

A solid sheet is preferably formed from a multilayer 30 (two or more layers) or a single layer structure.

A preferred single layer structure comprises nonwoven HTMF sheet or fabric which contains a TP. The TP may be present in a number of ways. It may simply be a powder which is interspersed between the fibers of the

aramid nonwoven sheet. The HTMF nonwoven sheet may contain TP (especially LCP) fibers (in other words the sheet is a mixture of TP fibers and HTMF fibers). The HTMF sheet may contain TP (especially LCP) pulps or mixtures of various forms of TP such as powders, fibers and/or pulps. Preferably the TP and the HTMF are both not an LCP, that is a lower melting LCP for the TP and a higher melting LCP for the HTMF. "Fiber-shaped" LCPs may be formed simply by wet pulping of pieces of LCPs such as pellets. For example the pellets are mixed with water, and if desired one or more surfactants, and the mixture subjected to relatively high shear mixing. If the shear applied is high enough the pellets will be broken up into LCP fiber-like particles.

If the solid sheet is formed from a multilayer structure, at least one of the layers must include a nonwoven HTMF sheet or fabric, and at least one of the layers must contain a TP (an "TP layer"). For example, if two layers are present, one could be an HTMF nonwoven sheet and the other could be either a nonwoven sheet of TP or a TP film. The HTMF nonwoven sheet could also contain TP, and/or vice versa. There may be more than one layer of a nonwoven HTMF sheet or fabric, and/or TP layer present.

Typically a TP layer will be about 20 to about 95 percent by weight, preferably about 30 to about 95 percent by weight, more preferably about 40 to about 95 percent by weight, and especially preferably about 70 to about 90 percent by weight, of the total weight of HTMF and TP in a multilayer structure. For example aramid papers typically weigh about 15 to about 200 g/m<sup>2</sup>.

In a TP layer, the TP may be present as a film, paper, short fiber, fiber, fibrid, fibril, or powder, or any combination of these. For example, because of the

tendency of solid LCPs to fibrilate when worked mechanically, combinations of the above forms when the LCP is in particulate form may be employed. TPs which are particulates and do not match any of the above 5 particulate definitions may also be used.

The amount of TP present in the single or multilayer structure must be sufficient to form a solid sheet product. Preferably, the TP will fill in essentially all the voids between HTMFs of the HTMF nonwoven sheet, as 10 well as any voids between other materials which may be present, such as fillers. Since nonwoven HTMF sheets or fabrics, especially papers, typically have about 10 to about 70 percent by volume void space, the single or multilayer structure to be consolidated into a solid 15 sheet will typically have at least about 20 percent by volume TP present, more typically about 30 to about 95 percent by volume present. The percent voids in a TP nonwoven sheet can be readily calculated by measuring its apparent density, and using the TP's measured (solid) 20 density. These calculation methods are well known.

Other materials may also be present in the single or multilayers, such as fillers, antioxidants, pigments, and/or other polymers, as long as the final sheet is solid.

25 Conditions (assuming the single or multilayer structure has enough TP present) for forming the first solid sheet are a combination of temperature (heating), pressure and the amount of time heating and pressure are applied. Generally, the higher the temperature applied, 30 the less the pressure needed and/or the less time needed. The higher the pressure, the lower the temperature needed and/or less time is needed. The longer the time used, the lower the temperature and/or the lower the pressure which may be needed. However, in most cases it may be

necessary to heat the TP to a temperature at least near its melting point. If too low a temperature, or too low a pressure, or too short a time, or any combination of these, is used, the TP may not flow enough to form a solid sheet. In this case, the temperature and/or pressure should be raised and/or the time increased. It is believed that the most important variable is temperature, particularly when approaching the melting point of the TP. Typically during the flowing of the TP (at high temperature and/or pressure) the HTMF is at least coated by, and in most instances, encapsulated by the TP. Although some of the "fibers" of the HTMF in the HTMF nonwoven sheet may be moved relative to one another, in the densified single or multilayer sheet the HTMF nonwoven sheet structure is still present.

While applying heat and pressure to form the first solid sheet, full or partial vacuum may also be applied to the single or multilayer structure to remove air or other gases dissolved in the materials of the single or multilayer structure or physically present in the structure, as between the HTMF and TP particulates. For example the single or multilayer structure may be placed in a vacuum bag or vacuum chamber and then heat and pressure applied. Using vacuum helps remove gases from the structure and avoid trapping gas bubbles (voids) in the first solid sheet. With any of the process variations described herein to consolidate the single or multilayer structure, use of vacuum is a preferred option.

A variety of methods can be used to apply both higher temperatures and pressures. A simple apparatus is a vacuum bag to which heat and pressure may be applied. A press or autoclave may also be used. A particularly preferred method is hot roll or hot belt calendering.

Temperatures, pressures, and time of treatment (contact) with the hot roll(s) or belt(s) can be controlled fairly well, as can the final thickness of the first sheet.

Calendering is a well known art, see for instance U.S.

5 Patent No. 3,756,908, which is hereby incorporated by reference in its entirety. To help ensure "complete" consolidation the calendering can be done in a vacuum.

The consolidation (applying heat and pressure) into a solid sheet may be carried out in one or more steps.

10 For example, more than one pair of calender rolls may be used to gradually consolidate the sheet to a solid structure. Each step may also be done individually, for example the sheet partially consolidated, and then consolidated in a second separate step.

15 Metal layers on one or both sides of the sheet may be applied in a single step process, or at any step of a multistep process. For example, the sheet may be partially consolidated by a pair of calender rolls or a press belt, metal sheets applied to one or both surfaces 20 of the sheet, and the consolidation finished in a second pair of calender rolls or another press belt.

It is preferred that the resulting sheet is "balanced" in the X-Y axes (sometimes referred to as the machine and transverse directions) in the plane of the 25 sheet. By balanced properties is meant that the tensile modulus and/or coefficient of thermal expansion (CTE) in one direction (machine or transverse) is no more than twice than, more preferably no more than about 20%, and especially preferably no more than about 10%, the tensile 30 modulus and/or CTE in the perpendicular direction. This is especially preferred when the TP comprises an LCP, and very preferred when the TP is an LCP (only). Sheeting formed by melt extrusion of TPs containing short random lengths of HTMFs (but no in nonwoven sheet form) tends to

have larger differences in tensile moduli and CTEs between the machine and transverse directions, especially if the TP is LCP. This is disadvantageous for use in circuit and other electronic board applications.

5 Any TP which has a low moisture absorption, such as perfluorothermoplastics [for example, polytetrafluoroethylene; copolymers of tetrafluoroethylene with hexafluoropropylene, perfluoro(vinyl ethers) such as perfluoro(methyl vinyl ether)], or ethylene; poly(ether-ether-ketones); poly(ether-ketone-ketones); and poly(ether-ketones); polyesters such as poly(ethylene terephthalate, poly(ethylene 2,6-naphthalate, and polyesters from bisphenol A and isophthalic/terephthalic acids;

10 15 polycarbonates especially those having higher temperature glass transition temperatures; poly 4-methylpentene; poly(aryl sulfides); poly(ether-imides); poly(aryl ethers); and LCPs are useful. Preferred TPs are perfluoropolymers, particularly those mentioned above,

20 25 and LCPs are especially preferred. Among the preferred properties for the TPs are very low moisture absorption, high melting point, low dielectric constant and low dielectric loss coefficient. LCPs have an excellent combination of such properties.

25 Useful LCPs include those which are described in U.S. Patent Nos. 3,991,013, 3,991,014 4,011,199, 4,048,148, 4,075,262, 4,083,829, 4,118,372, 4,122,070, 4,130,545, 4,153,779, 4,159,365, 4,161,470, 4,169,933, 4,184,996, 4,189,549, 4,219,461, 4,232,143, 4,232,144, 30 4,245,082, 4,256,624, 4,269,965, 4,272,625, 4,370,466, 4,383,105, 4,447,592, 4,522,974, 4,617,369, 4,664,972, 4,684,712, 4,727,129, 4,727,131, 4,728,714, 4,749,769, 4,762,907, 4,778,927, 4,816,555, 4,849,499, 4,851,496, 4,851,497, 4,857,626, 4,864,013, 4,868,278, 4,882,410,

4,923,947, 4,999,416, 5,015,721, 5,015,722, 5,025,082,  
5,086,158, 5,102,935, 5,110,896, 5,143,956, and  
5,710,237, each of which is hereby incorporated by  
reference in its entirety, and European Patent  
5 Application 356,226. Preferably the TP such as an LCP  
has a melting point of about 180°C or more, very  
preferably about 250°C or more, more preferably about  
300°C or more, and especially preferably about 325°C or  
more. Melting points are determined by ASTM D3418-82, at  
10 a heating rate of 20°C/min. The peak of the melting  
endotherm is taken as the melting point. These higher  
melting TPs will allow the circuit board to undergo high  
temperature processing with less possibility of warping,  
for example in reflow soldering. Low warpage is an  
15 important attribute of the boards used in circuit boards.  
LCPs are also particularly useful in this application  
since they have very low moisture absorption and also the  
permeability of LCPs to moisture is very low. Another  
preferred form of LCP is an aromatic polyester or  
20 aromatic poly(ester-amide), especially an aromatic  
polyester. By an "aromatic" polymer is meant that all of  
the atoms in the main chain are part of an aromatic ring,  
or are functional groups connecting those rings such as  
ester, amide, or ether (the latter of which may have been  
25 part of a monomer used). The aromatic rings may be  
substituted with other groups such as alkyl groups. Some  
particularly preferred aromatic polyester LCPs are those  
found in U.S. Patent Nos. 5,110,896 and 5,710,237. More  
than one LCP composition may be present in the first  
30 sheet, but one is preferred.

Useful HTMFs include as aramids,  
poly(phenylenebenzobisoxazole),  
poly(phenylenebenzobisimidazole),  
poly(phenylenebenzobisthiazole), poly(phenylene sulfide),

LCPs, and polyimide. When calculating the concentration of such fibers, the total of these types of fibers present will be used, for example the total of aramid and poly(phenylenebenzobisoxazole) fiber present. Among the 5 preferred properties are high modulus, high melting point and/or glass transition temperature and low moisture absorption.

Aramids are preferred HTMFs. Useful aramids include poly(p-phenylene terephthalamide), poly(m-phenylene 10 isophthalamide), and poly(p-phenylene/4,4'-oxydianiline terephthalamide). Preferred aramids are poly(p-phenylene terephthalamide), poly(m-phenylene isophthalamide), and poly(p-phenylene terephthalamide) is especially preferred. A description of the formation of aramid 15 (short) fibers, fibrils and fibrils of various types is found in U.S. Patent Nos. 5,202,184, 4,698,267, 4,729,921, 3,767,756 and 3,869,430, each of which is hereby incorporated by reference in its entirety. Description of the formation of nonwoven aramid sheets, 20 especially papers, is found in U.S. Patent Nos. 5,223,094 and 5,314,742, each of which is hereby incorporated by reference in its entirety. More than one aramid may be present in the first sheet.

The apparent density of the solid sheet is 25 preferably at least about 75% of its calculated density, more preferably at least about 80% of its calculated density, even more preferably at least about 90% of its calculated density, even more preferably at least about 95% of its calculated density, and even more preferably 30 at least about 98% of its calculated density.

When applying heat and pressure to form the solid sheet(s), metal layers, such as copper (or other metal) foil may be placed on the outer surface(s) (one or both) of the single or multilayer structure(s) to be

consolidated so that a metal clad laminate is produced. Often the metal layers are photolithographically etched to create circuit lines. Combinations of different single or multilayer structures may also be consolidated 5 together with or without metal layers.

The solid sheets, usually with metal layer(s) present may be used as the supporting "board" for circuit boards. Such boards may be formed by techniques known in the art, see for instance M. W. Jawitz, "Printed Circuit 10 Board Materials Handbook, McGraw-Hill Book Co., New York (1997). For example it is known how to coat LCPs (aside from consolidation with heat and pressure as described above) with metals (other than by using metal foils), see for instance U.S. Patent No. 5,209,819, incorporated 15 herein by reference in its entirety, European Patent Application 214,827, World Patent Application 9939021, and K. Feldmann, et al., Metallocberflaeche, vol. 51, p. 349-352 (1997).

Alternatively, solid sheets without metal layers may 20 first be formed and metal layers attached to one solid sheet or more than one solid sheet which have been plied up. Then metal layers may be attached to the outer surface(s). The assembly with metal sheets may be bonded together using heat and/or pressure, or adhesives may be 25 used.

If metal layers are present in and/or on the solid sheet, to measure the apparent density the metal layer can first be removed (as by acid etching) before measuring the apparent density, or the metal layers may 30 remain and their presence be taken into account by calculation, using their thickness and (known) density, when determining the apparent density of the solid sheet(s) present. If more than one layer of solid sheet is present [for example separated by metal layer(s)],

then the average apparent density (overall apparent density) of the solid sheet(s) present will be used as the benchmark for apparent density.

Circuit boards (including printed wiring boards and 5 printed circuit boards) produced from the above materials usually have low moisture absorption, and/or good high temperature resistance, and/or relatively low coefficients of thermal expansion, and/or low dielectric constant, and/or low warpage, an excellent combination of 10 properties for a circuit board. Once the substrate boards are formed they may be processed by normal methods to make circuit boards.

"Densified" sheets containing one or more layers may also be used in or as chip package substrates, chip 15 carriers and chip package interposers.

Procedure for Determining Equilibrium Moisture Absorption at 85°C and 85% relative humidity:

Five specimens (5 x 5 cm) of the same sample dried to a constant weight at 105°C are placed into a humidity 20 chamber set at 85°C and 85% relative humidity. After that, weight gain of the specimens is measured at each day. When an average weight gain for 3 consecutive days is less than 1 % of the total weight gain, specimens are deemed to be at equilibrium and average moisture 25 absorption (equal to the total weight gain) is calculated by dividing the total weight gain by the original weight of the sample and multiplying the result by 100.

EXAMPLES

The following Examples illustrate preferred 30 embodiments of our invention. Our invention is not limited to these Examples.

In the Examples, except as noted, all of the LCP used had the composition as that of Example 4 of U.S. Patent No. 5,110,896 derived from hydroquinone/4,4'-

biphenol/terephthalic acid/2,6-naphthalenedicarboxylic acid/4-hydroxybenzoic acid in molar ratio 50/50/70/30/320.

Also in the Examples herein the poly(m-phenylene isophthalamide) (PMIT) fibrils were made as described in U.S. Patent No. 3,756,908, which is hereby incorporated by reference in its entirety. The poly(p-phenylene terephthalamide) (PPTA) had a linear density of about 0.16 tex and a length of about 0.67 cm (sold by E.I. du Pont de Nemours and Company under trademark KEVLAR® 49).

Poly(ethylene terephthalate) (PET) fiber used: 2.1 dpf, 6 mm long, sold as Merge 106A75 by E. I. DuPont de Nemours & Co., Inc, Wilmington DE, U.S.A.

Glass fiber used: E-type glass fiber 6.5  $\mu\text{m}$  diameter and 6.4 mm long produced by Johns Manville Co., Denver, CO 80217, USA, sold as type M189.

Poly(phenylene oxide) (PPE) resin used was type 63D from the General Electric Co., Pittsfield, MA, U.S.A.

Polybenzoxazole fiber used: 1.5 dpf produced by Toyobo Co., Ltd. (Kita-ku, Osaka 530-8230, Japan) under trademark Zylon® (cut to length of 6.4 mm).

#### Example 1

The LCP used had the composition of the LCP of Example 9 of U.S. Patent 5,110,896, derived from hydroquinone/4,4'-biphenol/terephthalic acid/2,6-naphthalenedicarboxylic acid/4-hydroxybenzoic acid in molar ratio 50/50/85/15/320. The particulate LCP was prepared by grinding a melt blend mixture containing LCP (70 wt. %) and a polytetrafluoroethylene powder (30 wt. %) in a Bantam® Micro Pulverizer (model CF) along with liquid nitrogen until the particles passed through about a 10 mesh screen. The particles were reground in the same unit with additional liquid nitrogen until they passed through a 40 mesh screen.

Two (2.00) g of para-aramid fiber was placed in a standard laboratory pulp disintegrator (described in TAPPI Test Method T205 sp-95) together with 2500 g of water and agitated for 3 min. Independently, 69.13 g of an 5 aqueous, never-dried, meta-aramid fibrid slurry (0.43% consistency and freeness 330 ml of Shopper-Riegler) was placed in a same type of laboratory mixer together with 2.25 g of the above described particulate LCP and about 2000 g of water and agitated for 1 min. Both dispersions 10 were poured together into an approximately 21x21 cm handsheet mold and mixed with addition of about 5000 g of water. The resulting slurry had the following weight percent of solid materials:

meta-aramid fibrils 6.5%;  
15 para-aramid floc 43.5%;  
particulate LCP 50%.

A wet-laid sheet was formed. The sheet was placed between two pieces of blotting paper, hand couched with a rolling pin, and dried in a hand sheet dryer at about 20 190°C.

A piece 7.1 x 7.1 cm was cut from the dried sheet, covered on both sides with an aluminum foil treated with a mold release Mono-Coat® 327W (sold by Chem-Trend Inc.) and placed in the platen press MTP-20 (sold by 25 Tetrahedron Associates, Inc.) between two brass cover plates 1 mm thick each. The sheet was compressed in the press under the following conditions:

temperature 360°C, pressure 1.8 MPa for 2 min;  
temperature 360°C, pressure 89 MPa for 5 min;  
30 The press plates were then cooled with water while maintaining a constant pressure of 89 MPa. The final (compressed) sheet had a basis weight of 108.8 g/m<sup>2</sup>, thickness of 81.3 µm and an apparent density 1.34 g/cm<sup>3</sup>.

With a calculated density of about  $1.52 \text{ g/cm}^3$ , the sheet was about 88% of the calculated "solid" density.

Example 2

The final sheet (laminate) from Example 1 was placed  
5 between two sheets of copper foil ( $20 \mu\text{m}$  thick) and a metal-clad laminate was prepared by hot compression in the same press and using the same compression cycle as described in Example 1. The polymer portion (without copper foil) in the final metal-clad laminate had  
10 thickness  $78.7 \mu\text{m}$  and an apparent density of  $1.38 \text{ g/cm}^3$ , which was about 91% of the calculated "solid" density.

Example 3

Strand cut pellets of LCP were refined on a  $30.5 \text{ cm}$  diameter Sprout-Waldron type C-2976-A single rotating  
15 disc refiner equipped with plates in one pass with the gap between plates of about  $25 \mu\text{m}$ , a feed speed of about  $60 \text{ g/min.}$  and continuous addition of water in quantity of about  $4 \text{ kg}$  of water per  $1 \text{ kg}$  of the pellets. The resulting LCP pulp was additionally refined in a Bantam®  
20 Micropulverizer, Model CF, to pass through a 30 mesh screen. A water slurry was prepared by mixing LCP pulp and poly(p-phenylene terephthalamide) floc. The slurry had the following percentages (as a percent of total  
solids) of solid materials:

25 LCP pulp 65%;  
poly(p-phenylene terephthalamide) floc 35%.

A continuous sheet was formed from the slurry on a Rotonier (combination of Rotoformer and Fourdrinier) papermaking machine equipped with a horizontal thru-air  
30 drier. The headbox consistency was about 0.01%, forming speed about  $5 \text{ m/min}$  and temperature of air in the drying section of about  $338^\circ\text{C}$ . The formed paper was calendered at ambient temperature between two metal rolls  $86 \text{ cm}$

diameter each at a speed of about 7 m/min. and linear pressure of about 6500 N/cm.

Calendered material had basis weight of about 72.5 g/m<sup>2</sup> and apparent density of about 0.82 g/cm<sup>3</sup>, which 5 corresponded to about 57 % from calculated density.

Tensile modulus in the machine direction was 2.52 GPa and in the transverse direction 1.65 GPa. Ten plies of calendered sheet (51 x 51 cm each) were placed between two sheets of 17  $\mu\text{m}$  thick copper foil and compressed in a 10 platen press at the following conditions: 348°C - 2.6 MPa - 1 min >> 348°C - 34 kPa - 1 min >> 348°C - 2.6 MPa - 1 min >> 149°C - 2.6 MPa - 1 min. The thickness of the final copper clad laminate was 0.541 mm, which corresponded to 0.507 mm thickness of polymeric material 15 (the rest was the copper foil). Based on basis weight of 10 plies of calendered material loaded in the press (725 g/m<sup>2</sup>) and thickness of polymer material in the final laminate (0.507 mm), apparent density of polymer material in the final copper clad laminate was estimated to be 20 1.43 g/cm<sup>3</sup>, which corresponded to about 99% of the calculated density. After etching of copper foil, CTE in plane was determined as being in the range of +/- 1 ppm/°C.

#### Example 4

25 Strand cut pellets of LCP were refined on 30.5 cm diameter Sprout-Waldron type C-2976-A single rotating disc refiner equipped with plates in one pass using a gap between plates of 25  $\mu\text{m}$ , feeding speed of about 60 g/min. and continuous addition of water in quantity of about 4 30 kg of water per 1 kg of the pellets. This LCP pulp was additionally refined in a Bantam® Micropulverizer, Model CF, to pass through a 60 mesh screen. The slurry was prepared by mixing the LCP pulp with poly(p-phenylene terephthalamide) floc. The resulting slurry had the

following percentages (as a percent of total solids) of solid materials:

LCP pulp 90%;

poly(p-phenylene terephthalamide) floc 10%.

5 A continuous sheet was formed from the slurry on a Rotonier (combination of Rotoformer and Fourdrinier) papermaking machine equipped with horizontal thru-air drier.

The headbox consistency was about 0.01%, forming speed 10 about 5 m/min and temperature of air in the drying section of about 338 C. The formed material was calendered at ambient temperature between two metal rolls 4 cm diameter each at speed about 5 m/min. and linear pressure of about 2000 N/cm. Calendered material had a 15 basis weight of 66.1 g/m<sup>2</sup> and apparent density about 0.66 g/ml which corresponded to about 46% of the calculated density. Its tensile modulus in the machine direction as 1.30 GPa, and about 0.93 GPa in the transverse direction. Ten plies of calendered sheet were placed between two 20 sheets of 17  $\mu$ m thick copper foil and compressed in the platen press under the following conditions: 348°C - 0.87 MPa - 1 min >> 348°C - 34 kPa - 1 min >> 348°C - 0.87 MPa - 1 min. >> 149°C - 0.87 MPa - 1 min. Density of 25 polymeric material in the final copper clad laminate was 1.39 g/cm<sup>3</sup>, which corresponded to about 96.5% of the calculated density. The CTE 23 ppm/°C in the machine direction and 33 ppm/°C in the transverse direction. Moisture absorption was 0.4 wt. %.

Example 4

30 Sheets (25 cm x 21 cm) of THERMOUNT® reinforcement type 2N710 available from I.E. DuPont de Nemours & Co., Wilmington, DE, U.S.A., which is an aramid paper containing a majority of PPTA floc with some poly(m-phenylene isophthalamide fibrils) were impregnated in two

steps with a water dispersion of Teflon® PFA [a thermoplastic copolymer of tetrafluoroethylene and perfluoro(propyl vinyl ether) available from E. I. DuPont de Nemours & Co., Wilmington, DE, U.S.A]. Each 5 impregnation was conducted in a bath having about 60% solids, followed by squeezing between two glass rods and drying in an oven at 105°C. PFA content in the final impregnated sheets was about 77 wt. %. Impregnated sheets were consolidated by compression in 2 plies in a 10 platen press under the following conditions: 316°C - 3.9 MPa - 5 min. >> 149°C - 3.9 MPa - 1 min. Consolidated sheets had basis weight 80.9 g/m<sup>2</sup>, thickness 0.145 mm and apparent density 1.82 g/cm<sup>2</sup>, which corresponded to 91% of the calculated density. Three 15 consolidated sheets were compressed together between two sheets of copper foil 17 µm thick each at the following conditions: 316°C - 3.9 MPa - 10 min >> 149°C - 3.9 MPa - 1 min. In the final copper clad laminate, apparent density of polymeric material was about 1.88 g/cm<sup>2</sup>, which 20 corresponded to 94% of the calculated density. Moisture absorption of this material at 85°C and 85% relative humidity was 0.7 wt. %.

Example 5

One g of polybenzoxazole (PBO) fiber was placed in a 25 laboratory mixer (British pulp evaluation apparatus) with 2500 g of water and agitated for 3 min. Independently, 69.77 g of an aqueous, never-dried, poly(m-phenylene isophthalamide) fibrid slurry (0.43% consistency and freeness 330 ml of Shopper-Riegler) was placed in the 30 same type of laboratory mixer together with 1.70 g of LCP pulp (passed through a 30 mesh screen after grinding in a Bantam Micropulverizer) and about 2000 g of water and agitated for 1 min. Both dispersions were poured together into an approximately 21x21 cm handsheet mold

and mixed with addition of about 5000 g of water. The resulting slurry had the following percentages (of total solids) of solid materials:

5 poly(m-phenylene isophthalamide) fibrils 10%;  
PBO floc 33%;  
LCP pulp 57%

A wet-laid sheet was formed. The sheet was placed between two pieces of blotting paper, hand couched with a rolling pin, and dried in a hand sheet dryer at about 190°C. The dried sheet had basis weight of about 68.8 g/m<sup>2</sup>. The dried sheet was consolidated by calendering at ambient temperature between two metal rolls 10 cm diameter each at a linear pressure of about 2000 N/cm and speed about 5 m/min. The calendered sheet had density of about 0.69 g/cm<sup>3</sup>, which corresponded to about 48 % of the calculated density. The sheet was placed between two sheets of 17  $\mu$ m thick copper foil and compressed in a platen press at the following cycle: 343°C - 0.21 MPa - 1 min >> 343° C - 33.1 MPa - 2 min >> 93°C - 33.1 MPa - 1 min. Polymeric material in the final copper clad laminate had apparent density of about 1.34 g/cm<sup>3</sup>, which corresponded to about 93 % of the calculated density.

### Example 6

Poly(p-phenylene terephthalamide) fiber (0.84 g) was placed in a laboratory mixer (British pulp evaluation apparatus) with 2500 g of water and agitated for 3 min. Independently, 65.12 g of an aqueous, never-dried, poly(m-phenylene isophthalamide) fibrid slurry (0.43% consistency and freeness 330 ml of Shopper-Riegler) was placed in the same type of laboratory mixer together with 1.68 g of PET floc and about 2000 g of water and agitated for 1 min. Both dispersions were poured together into an approximately 21x21 cm handsheet mold and mixed with addition of about 5000 g of water. The resulting slurry

had the following percentages (of total solids) of solid materials:

poly(m-phenylene isophthalamide) fibrils 10%;  
poly(p-phenylene terephthalamide) floc 30%;  
5 poly(ethylene terephthalate) floc 60%

A wet-laid sheet was formed. The sheet was placed between two pieces of blotting paper, hand couched with a rolling pin, and dried in a hand sheet dryer at about 190°C. The dried sheet had basis weight of about 67.0  
10 g/m<sup>2</sup>. Another sheet was prepared by exactly the same procedure. Both sheets were placed together between two sheets of aluminum foil with mold release on their surfaces (see example 1) and compressed in the platen press at the following cycle: 266°C - 0.21 MPa - 2 min >>  
15 266°C - 15.9 MPa - 2 min >> 93°C - 15.9 MPa - 2 min. The consolidated sheet had an apparent density of about 1.28 g/cm<sup>3</sup>, which corresponded to about 91% of the calculated density.

#### Comparative Example A

20 Aramid paper with basis weight of 31 g/m<sup>2</sup> and a density of 0.64 g/ml made from 87% by weight PPTA floc (2.25 denier per filament, 6.7 mm cut length) and 13% by weight poly(m-phenylene isophthalamide) fibrils was prepped with commercial multi-functional epoxy system  
25 L-1070 as in Example 2. Thirty-two preps made by the above process were further laminated between two Cu sheets (17 µm thick) under the following conditions in a vacuum press:

- 30 (a) Held for 1 h in vacuum (no external pressure or temperature).
- (b) Heated to 200°C (5°C/min) from ambient temperature under a pressure of 6.9 MPa.
- (c) Held for 1 h at 200°C and 6.9 MPa.

(d) Cooled to room temperature fast (water quench on platens) under pressure

Epoxy resin content in the polymer portion of the final laminate was about 53% wt. %. After etching of 5 copper foil, properties of polymer portion of the laminate were measured. CTE  $\epsilon$  was about 14.2 ppm/ $^{\circ}$ C in the machine direction and 12.1 ppm/ $^{\circ}$ C in the transverse direction, and moisture absorption at 85 $^{\circ}$ C and 85% humidity was about 2.1 wt. %.